Catalytic Gold

APPLICATIONS OF ELEMENTAL GOLD IN HETEROGENEOUS CATALYSIS

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Although gold as been little used in heterogeneous catalysis hitherto, the metal shows some very interesting properties which ensure continued study of it for this field. In particular its remarkably high selectivity in some reactions and striking activity in oxygen transfer catalysis have received significant attention.

Compared to the noble metals in group VIII and the other metals in group IB of the periodic table, gold has found very little application as a heterogeneous catalyst. This comes as no surprise in view of the inert character of gold and its limited affinity for gas adsorption. Gold has a completely filled 5 *d* electron shell. Its lone 6 *s* electron experiences less screening from the nucleus through the 5 *d* electrons compared to alkali metals, resulting in a significantly higher ionization potential. The 5 *d* electron levels are only slightly lower in energy than the 6 *s* level. This accounts for the possibility of reaching higher oxidation states of gold than Au^{+1}, in particular Au^{+3}. These oxidation states can be stabilized via ligands, or, under certain conditions, via partially covalent bonds between gold and oxide lattices. The latter situation might be of importance in cases where quite unusual catalytic activities of gold are reported, especially in the context of oxygen transfer reactions.

In a photoelectron spectroscopic study of gold/alumina catalysts, evidence for the existence of Au^{+1} was found after pretreatment of $AuCl_3 - Al_2O_3$ with oxalic acid at temperatures of up to 110°C (1). Mössbauer spectroscopy of a gold/γ-alumina catalyst treated at 370°C indicated the presence of a gold species having an isomer shift more negative than that of zero valent gold (2). This result was interpreted in terms of a lower *s* electron density at the gold nucleus than that of gold metal due to a strong electronegative environment in the gold/alumina sample. Incidentally, this gold/alumina catalyst proved to be quite active for the oxidation of carbon monoxide to carbon dioxide by nitrous oxide.

In X-ray adsorption fine structure spectroscopy (EXAFS) studies of gold/γ-alumina and gold/magnesia catalysts, (3, 4) two distinct phases of gold were found. Part of the gold was structurally similar to metallic gold; the rest was present in the form of either two-dimensional or atomically dispersed clusters, carrying a formal charge of +1. Such differences in electron density on certain gold surface sites might play a crucial role in rendering gold catalytically active despite its inert character in the bulk metallic state.

Gold as a Hydrogen Transfer Catalyst

It is well documented that gold is not capable of chemisorbing detectable quantities of molecular hydrogen at room temperature (5-8) due to the high activation energy required for dissociative adsorption of hydrogen (9). At higher temperatures, however, atomic hydrogen formation proceeds via a first order reaction having an activation energy of 71 to 75 kJ/mole (10, 11).

Consequently, gold catalyzes the isotopic exchange reaction between hydrogen and deuterium (4, 6, 12, 13, 32) and also the $o\text{-}H_2/p\text{-}H_2$ conversion (14, 15).

$$H_2 + D_2 \rightleftharpoons 2HD \qquad (1)$$

$$o\text{-}H_2 \rightleftharpoons p\text{-}H_2 \qquad (2)$$

The catalytic activity of gold for hydrogen – deuterium exchange can be enhanced even at low temperatures by supplying atomic hydrogen directly to the gold surface (12, 16), as shown in Figure 1. Above 27°C the recombination of atomic hydrogen on a gold catalyst proceeds according to Kislyuk and Tret'yakov (17) via the Langmuir-Hinshelwood mechanism involving two hydrogen atoms that are adsorbed on adjacent gold sites. At lower temperatures, (−70°C), adsorbed hydrogen atoms recombine to form molecular hydrogen with gas phase hydrogen atoms via the Eley-Rideal mechanism (17).

In a recent study of the hydrogen-deuterium exchange on gold supported on poly(tetrafluoroethylene), an exchange mechanism was postulated involving molecularly adsorbed hydrogen and deuterium and a dimeric reaction intermediate (18).

As early as 1925, gold powders were found to be active catalysts for the hydrogenation of ethylene (19),

$$H_2C{=}CH_2 + H_2 \longrightarrow H_3C{-}CH_3 \qquad (3)$$

and to this day, olefin hydrogenation remains one of the major catalytic applications of gold (20, 21). Interestingly, hydrogenation of olefins such as 1-pentene to *n*-pentane occurs without simultaneous isomerization due to double-bond migration (21, 22). This surprisingly high selectivity sets gold apart from all other metals known to catalyze olefin hydrogenation. Butadiene and butyne, in turn, were selectively hydrogenated to olefin products without any significant alkane formation (23). This unusual behaviour makes gold an interesting catalyst for the hydrogenation of natural oils. No reports on the use of gold for this purpose have, however, been noted. The hydrogenation activity of gold/silica and gold/alumina catalyst per unit weight of gold increased as the metal loading decreased from 5 to 0.01 per cent probably due to an increase in gold dispersion with decreasing metal content (24).

Gold is known also to catalyze both the hydrogenation and dehydrogenation of cyclic hydrocarbons. Tetenyi and Schachter found that gold was capable of dehydrogenating cyclohexane (25). The catalytic function of gold seems to be reversible and cyclohexene could be hydrogenated to produce cyclohexane when atomic

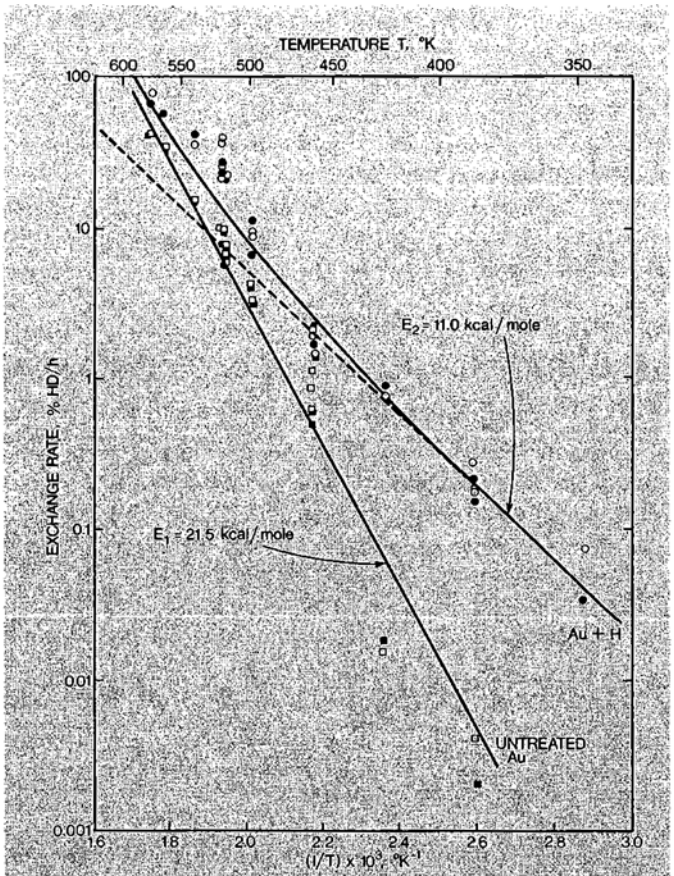
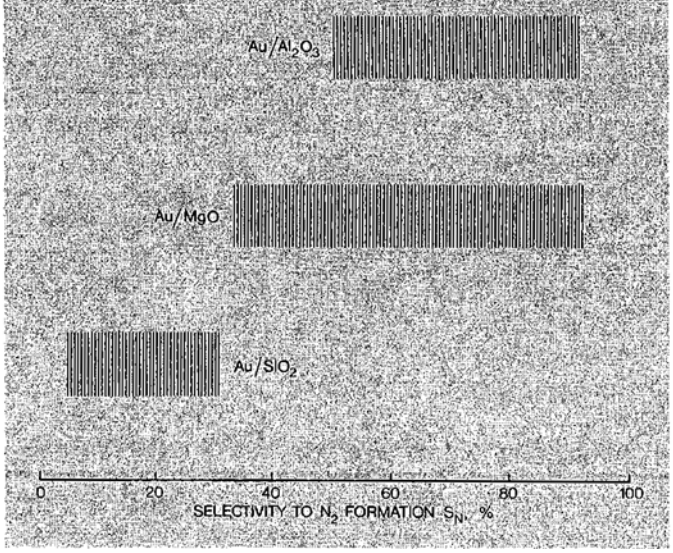


Fig. 1 H_2-D_2 exchange rate on gold foil with a geometric surface area of 500 cm^2/g as a function of temperature. Circles denote the results on gold exposed to atomic hydrogen prior to the exchange reaction; squares denote the results on untreated gold. After (12)

Fig. 2 Selectivity to N_2 formation (S_N) for reactions (5) and (6) on supported gold at 350 °C with $3 \leq P_{H_2}/P_{NO} \leq 5$ and a total pressure of 100 kPa. After (32)



hydrogen was supplied to the gold surface via diffusion through palladium-silver (26, 27).

In the absence of hydrogen, cyclohexane is readily dehydrogenated to benzene; the latter becomes the main reaction product in the presence of traces of oxygen (28). In this context, gold seems superior to platinum because of the weak chemisorption of oxygen and hydrocarbon species on its surface. Benzene formation is not only favoured by decreasing hydrogen partial pressures, but also by increasing temperatures (29).

To get better insight into the details of the interaction of gold surfaces with hydrogen donor and acceptor molecules, Parravano studied the hydrogen transfer between cyclohexane and benzene using isotopic carbon tracer (30, 31):

$$^{14}C_6H_{12} + C_6H_6 \rightleftharpoons {}^{14}C_6H_6 + C_6H_{12} \qquad (4)$$

Parravano concluded that under the reaction conditions the gold surface was preponderantly covered by adsorbed hydrogen and that the surface coverage by hydrocarbon fragments was negligible. The hydrogen adsorption was considered to be weak and delocalized (31).

The remarkable catalytic activity of gold for hydrogen transfer reactions prompted Galvagno and Parravano to study the reduction of nitric oxide by hydrogen over gold catalysts on three different supports, namely silica, alumina and magnesia (32,4). The activity of these gold catalysts for nitric oxide reduction was astonishingly high. Turnover numbers of up to 10^{-2} molecules of nitric oxide per gold surface site per second were obtained at a temperature of 350°C. A striking influence of the nature of the support was discovered (Figure 2). On gold/alumina, the main reaction product was nitrogen, formed according to the following equation:

$$2\,NO + 2H_2 \longrightarrow 2\,H_2O + N_2 \qquad (5)$$

Gold/magnesia catalysts showed slightly lower selectivity for nitrogen formation. Gold/silica catalysts, however, formed ammonia preferentially as shown below:

$$2\,NO + 5\,H_2 \longrightarrow 2H_2O + 2\,NH_3 \qquad (6)$$

The selectivity effect was explained by differences in electron density on the gold sites allowing different amounts of electron backdonation into antibonding π-orbitals in the adsorbed nitric oxide. This, in turn, should result in various degrees of destabilization of the N-O bond. A weakened N-O bond was believed to lead to nitrogen formation via dissociative chemisorption of nitric oxide, while an associative chemisorption of nitric oxide was responsible for the formation of ammonia. The modification of the electron density on the gold sites was related to the electron-donating or accepting properties of the oxide supports employed.

In a subsequent stuctural study of gold/silica and gold/alumina catalysts by small angle X-ray scattering, X-ray absorption

spectroscopy and transmission electron microscopy (4) evidence for an electronic interaction between gold and alumina, but not between gold and silica, was detected. The EXAFS data presented, however, did not allow the drawing of definite conclusions with regard to the formal oxidation state of the gold sites that were active for the reduction of nitric oxide.

Gold seems to be able to catalyze not only the reduction of nitric oxide, but also that of the carbonyl group in acetone. The main product of the reaction between acetone and hydrogen on evaporated gold films was isopropanol, formed by addition of two hydrogen atoms to the carbonyl bond (33, 34). The activity of gold for the reduction of the carbonyl group was substantially lower than that of other metals and was by no means as spectacular as in the case of the nitric oxide reduction. It should be noted that the unusual activity for nitric oxide reduction might have been due to support interactions which were, of course, absent in the case of the gold films used for the reduction of acetone.

Besides catalyzing the reduction of the N-O and C-O bond, gold is also an active catalyst for the fission of the C-N bond. The reaction of ethylamine with hydrogen in the presence of evaporated gold films produced mainly ammonia and diethylamine (35). A remarkable activity of gold for the hydrocracking of polyethylene was reported by Legate and Sermon (36). Polyethylene, used as support for gold particles was cracked at temperatures between 20 and 480°C at rates far exceeding those achieved by platinum. The authors argued that the reaction was initiated by hydrogen spillover from the metal to the polymer support.

Skeletal Rearrangements on Gold Catalysts

It is not uncommon for gold to catalyze skeletal rearrangements of hydrocarbons, and these are sometimes accompanied by dehydrogenation. Even in the absence of hydrogen, gold was found to catalyze the isomerization of 1-butene to 2-butene giving *cis* and *trans* isomers in the equilibrium ratio (37). Even though gold was rather inactive for the hydrogenolysis of neopentane compared to group VIII metals, it was one of the few metals (together with iridium and platinum) capable of isomerizing neopentane to isopentane with comparable selectivity (38) as shown in Figure 3. This isomerization activity was attributed to the high electronegativity of gold, iridium and platinum and the possibility of variations in the surface valency as a result of the promotion of *d* electrons into empty *s* levels.

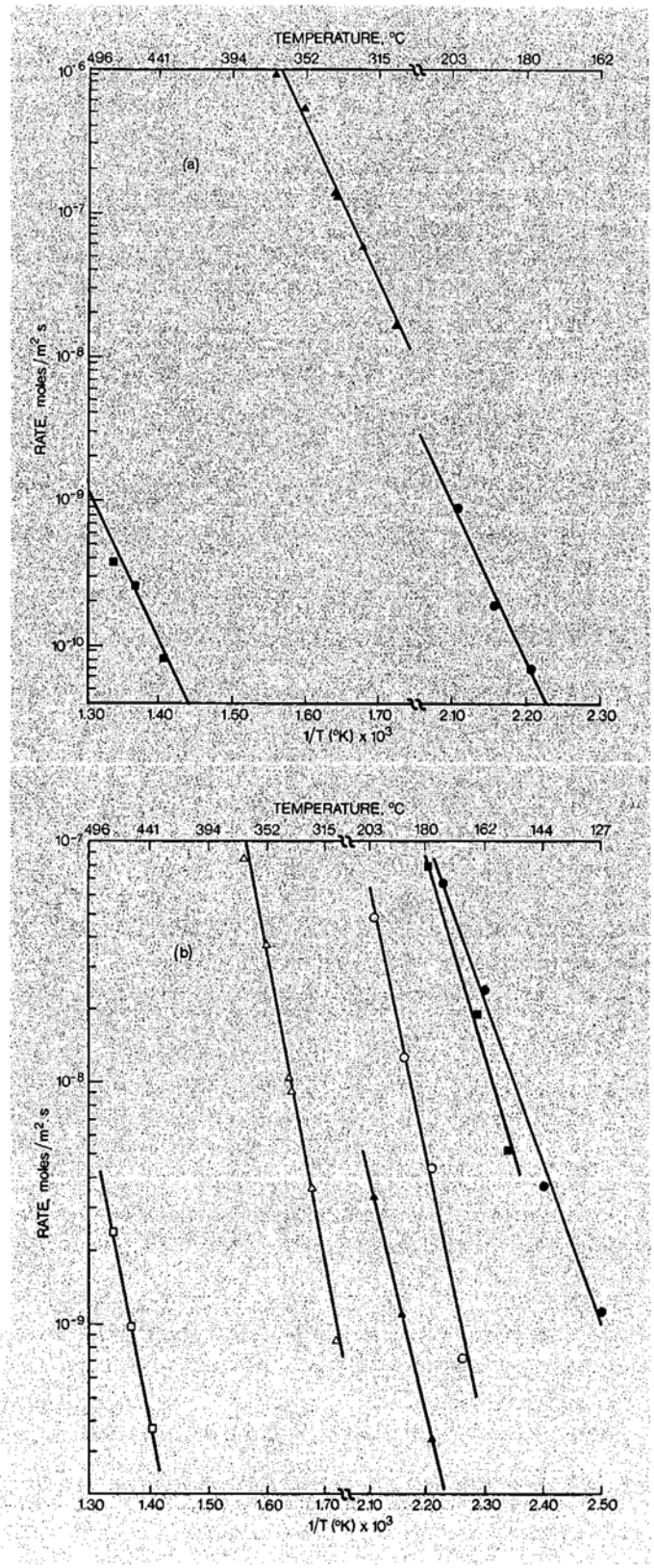
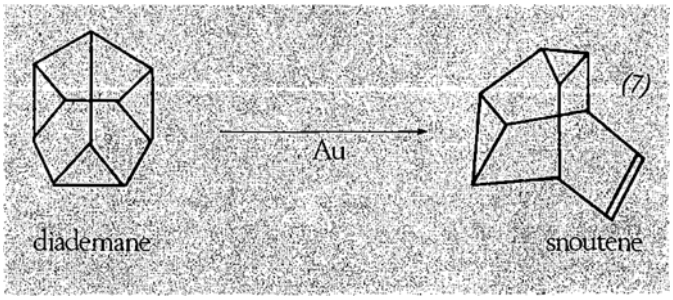


Fig. 3(a) Arrhenius plots for the isomerization of neopentane under differential reactor conditions. Total pressure = 100 kPa and the hydrogen:neopentane ratio = 10:1. The code for the experimental points is ▲ = 1% Pt/Spheron; ● = 10% Ir/SiO_2; ■ = Au powder. After (38)

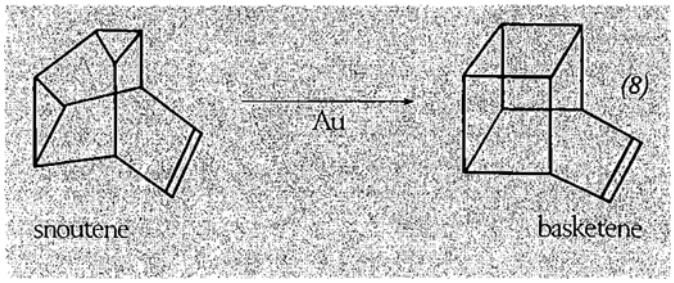
Fig. 3(b) Arrhenius plots for the hydrogenolysis of neopentane. Experimental points ● = 10% Os/SiO_2; ■ = 5% Ru/SiO_2; ○ = 5% Rh/SiO_2; ▲ = 10% Ir/SiO_2; ▲ = 1% Pt/Spheron; □ = Au powder. After (38)

Dimethyl- and diethylcyclopropane were found to isomerize on gold at a temperature of 375°C with breaking of the cyclopropane ring at the most substituted carbon atom, in contrast to Group VIII metals with which hydrogenolysis of cyclopropane took place with cleavage of the ring at the C-C bond opposite the substituted carbon atom (39). In a patent (40), geminally substituted cycloalkanes, such as 1,1-dimethylcyclohexane, were isomerized in the presence of gold-sodium/alumina catalysts to give 1,2-dimethylcyclohexane and ethylcyclohexane. A subsequent patent claimed the production of alkyl aromatic compounds by heating geminally substituted cycloalkanes in the presence of gold-containing catalysts (41).

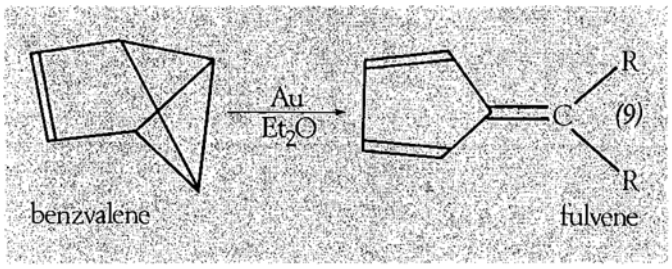
An interesting gold catalyzed rearrangement of strained ring hydrocarbons is reported by Meyer and de Meijere (42). For example, diademane rearranged to give snoutene according to reaction (7):



At higher temperatures, snoutene rearranged further to yield basketene (reaction (8)):



Similarly, benzvalene isomerized to fulvene in the presence of gold metal (43) according to reaction (9):



Parravano investigated the ability of gold to catalyze alkyl transfer between benzene and toluene (44) using ^{14}C-labelled compounds. At 390°C, gold was found to be comparable in activity with platinum and iridium, and significantly more active than ruthenium (Table I). The activity of gold seemed to be strongly influenced by the catalyst preparation method. Gold catalysts prepared via reduction of gold salts with formaldehyde were four times more active than catalysts prepared by thermal decomposition. The alkyl transfer activity of gold catalysts has been the basis of patent applications (45, 46).

While alkanes are generally not chemisorbed on gold, silanes can form coordinative bonds with metals having full *d*-bands. Methylsilane chemisorption on gold was found to be accompanied by evolution of methane and hydrogen (47). At temperatures as low as −78°C, hydrogen atoms in the silyl group underwent isotopic exchange with deuterium stemming from CH_3SiD_3 (47, 48). The specific activity of gold for this reaction exceeded that of nickel, rhodium, tungsten and molybdenum.

Gold as Oxygen Transfer Catalyst

While the hydrogen transfer capability of gold catalysts is, with a few exceptions, rather marginal compared with that of other noble metals, the picture changes drastically in the case of oxygen transfer reactions. In this area, striking activities are encountered, often comparable with those of other metals.

Let us first consider in more detail oxygen chemisorption on gold. Molecular oxygen was found to chemisorb on gold powder over a wide temperature range, with two distinct maxima at −50°C and at 200°C, respectively in the adsorption isobar (49) (Figure 4). The low temperature species was firmly chemisorbed and could not be removed by evacuation. In fact, Chesters and Somorjai reported that a chemisorbed oxygen species was stable *in vacuo* up to 800°C (50). These findings are in line with the existence of a relatively large heat of adsorption of oxygen on gold (51). However, some controversy still exists as to the endothermic or exothermic nature of the chemisorption of oxygen on gold (52, 53). While the adsorption of oxygen on gold films was found to be irreversible in the temperature range of 295-405°C (54), oxygen chemisorbed on gold/magnesia could be completely desorbed at 400°C and the temperature had to be lowered to 200°C to achieve irreversible chemisorption (55). At this lower temperature, oxygen chemisorption appeared to be a good method of determining the dispersion of supported gold catalysts, using a stoichiometry of one oxygen molecule per four gold atoms (55). Use of microwave-excited oxygen allows chemisorption to occur at room temperature (56). At temperatures above 800°C, oxygen seems to chemisorb dissociatively on gold surfaces (57).

Gold has not found significant commercial application as or in oxidation catalysts, despite its considerable activity especially for oxidative dehydrogenation. A recent review compared gold as an oxidation catalyst with copper and silver (58). Methanol is dehydrogenated to formaldehyde on gold catalysts (59-61). It seems

that weak adsorption of oxygen on gold prevents the full oxidation to carbon dioxide, making gold a highly selective catalyst for oxidative dehydrogenation (62). Not only methanol, but also higher alcohols can undergo oxidative dehydrogenation to aldehydes in the presence of gold catalysts (63-68). Secondary alcohols are converted to ketones (65) while calcium bifluoride proved to be the most suitable support for gold dehydrogenation catalysts (63). There are numerous patent claims concerning oxidative dehydrogenation on gold catalysts, including the dehydrogenation of ethyleneglycol to glyoxal (69), of cyclohexanone to cyclohexenone (70), of ethylpyridine to vinylpyridine (71), of ethylbenzene to styrene (72), and of methyl esters of saturated aliphatic carboxylic acids to methyl acrylate and methacrylate (73).

Table I
Values of the Rate Constant, k_r for the Alkyl Transfer Between Benzene and Toluene at 390°C on Supported Metals (after (44))

Catalyst	Preparation Method	Metal wt. %	k_r X 10^7 mole/$g_{(cat.)}$ s.atm.
Ru/Al_2O_3	Impregnation, thermal decomposition	2.0	0.02
Ir/Al_2O_3	Impregnation, thermal decomposition	0.7	0.19
Pt/Al_2O_3	(commercial sample)	0.4	0.19
Au/Al_2O_3	Impregnation, thermal decomposition	0.3	0.14
Au/Al_2O_3	Impregnation, reduction with HCHO	0.3	0.58
Au/MgO	Impregnation, reduction with HCHO	2.0	0.35

It has been known for a long time that gold surfaces are capable of catalyzing the oxidation of carbon monoxide to carbon dioxide (74). Cha and Parravano studied extensively the redistribution of isotopic carbon between these two gases on supported gold catalysts (75) in order to determine the affinity of gold for oxygen stemming from molecules other than molecular oxygen. The rate constant for the reaction

$$*CO_{2(g)} + CO_{(g)} \longrightarrow CO_{2(g)} + *CO_{(g)} \qquad (10)$$

on supported gold catalysts is compared to other metals in Table II. The activity of gold decreased with the increasing partial pressure ratio P_{CO_2}/P_{CO}. This trend was interpreted in terms of reduced surface gold atoms as active sites for the exchange reaction. It was found that the degree of gold dispersion influenced the rate of reaction, indicating a correlation between the gas mean free path and the particle diameter. A decrease in gold particle size resulted in increased affinity of the gold surface for oxygen. The isotopic exchange reaction between carbon monoxide and carbon dioxide seemed to be accelerated in the presence of hydrogen or water vapour (76). It also appeated that the nature of the support had a decisive influence on the catalytic activity of gold; magnesia- and alumina-supported gold were more active by more than one order of magnitude for the oxygen transfer between carbon monoxide and carbon dioxide than silica-supported gold (77). The kinetics of the catalytic oxidation of carbon monoxide at temperatures between −23 and 60°C indicated that adsorption of both reactants occurred on the gold surface (78). Adsorption of carbon monoxide on gold is substantiated by infrared spectroscopic investigations showing a single band between 2120 cm^{-1} and 2070 cm^{-1} (79-82). In the presence of oxygen, the intensity of the carbon monoxide band decreased and oxidation of the adsorbed species to carbon dioxide occurred (79, 82). Hennig reported the ability of colloidal gold metal particles placed on graphite single crystals to catalyze the oxidation of graphite to carbon dioxide (83). The catalytic action seemed to occur at the graphite-metal interface.

In contrast to the oxidation of carbon monoxide where both reactants appear to be adsorbed on the gold surface, the gold-catalyzed oxidation of hydrogen was found to be controlled by collision of molecular hydrogen with adsorbed oxygen (84).

The unique selectivity of silver for partial oxidation of olefins leading to the formation of epoxides prompted numerous olefin oxidation studies on gold catalysts. Partial olefin oxidation seems to

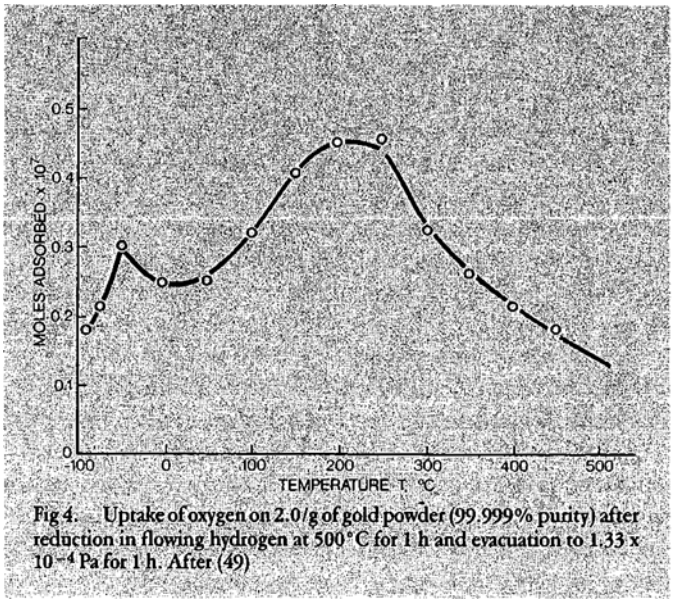


Fig 4. Uptake of oxygen on 2.0/g of gold powder (99.999% purity) after reduction in flowing hydrogen at 500°C for 1 h and evacuation to 1.33 x 10^{-4} Pa for 1 h. After (49)

Table II
Rate Constant, k, for Reaction (10) Catalyzed by Supported Metals *(after (75))

Catalyst		Temperature, °C	k, $mole/g_{(cat.)}.s.atm.$
Metal	Metal, wt %		
Au	0.3	350	$2.5x10^{-7}$
Au	0.7	350	$3.6x10^{-7}$
Au	2.0	350	$6.8x10^{-6}$
Au	5.0	350	$4.9x10^{-7}$
Pt	1.0	356	$6.7x10^{-10}$
Pt	1.0	405	$3.1x10^{-9}$
Ru	1.0	350	$1.5x10^{-7}$

*Au catalysts supported on MgO and prepared by reduction; Pt, Ru supported on Al_2O_3 and prepared by decomposition of the metal salt

be related to both the relative strength of the metal-oxygen bond (85) as well as to the mechanism of olefin adsorption (58, 87, 88). Consequently, gold shows less potential for partial oxidation than silver and catalyzes in many instances the full oxidation to carbon dioxide. In fact, gold behaves more like copper (I) oxide than silver (58). Ethylene is oxidized mainly to carbon dioxide and water with traces of acetic acid and acetaldehyde (86). Manara and Parravano (87) proposed an adsorption of ethylene on gold involving two surface sites per molecule, favouring fragmentation of ethylene, in contrast to silver where single-site adsorption of ethylene provides the necessary intermediate for ethylene oxide formation.

A similar mechanism was found to be at work in a study of oxygen transfer between propylene and propylene oxide (88). Cant and Hall (86) reported that propylene oxidation on gold sponge and on gold/silica led to up to 50 per cent acrolein and 3 per cent acetone. Gold/alumina showed much lower selectivity for these products. The rate determining step in acrolein formation was the abstraction of hydrogen leading to an allylic intermediate (86). A rather surprising 50 per cent selectivity in favour of production of propylene oxide was reported for the oxidation of propylene on gold catalysts prepared by decomposition of gold ketenide (89). Differences in surface structure, including defects and high energy regions, were held responsible for the unusual catalytic activity. A similar high selectivity for production of propylene oxide was achieved by applying hot-electron flow through gold surfaces during the oxidation of propylene (90, 91). There is also a number of patent claims with regard to the conversion of other olefins to epoxides (92). However, in these cases the claims include both silver and gold, and it is not clear to what extent pure gold was found to be active.

While Van Ham *et al.* reported that gold was totally inactive for the catalytic oxidation of cumene to cumene hydroperoxide (93), a remarkably high selectivity of metallic gold for hydroperoxide formation, albeit at very low activity compared to other metals, was found by other authors (94) in the liquid-phase oxidation of cumene. In contrast to copper and silver, no acetophenone was formed. Gold was found to exhibit weak catalytic activity for the oxidation of sulfur dioxide to sulfur trioxide (95, 96). Chemisorbed sulphur trioxide seems to be formed on the gold surface.

The fact that the nature of the gold catalysts and especially the type of support played such a crucial role in determining the catalytic activity of gold in reactions of oxygen-bearing molecules prompted an investigation of metal-support interactions in supported gold catalysts (97). In particular, it appeared to be important to check whether impregnation of typical catalyst supports such as silica and magnesia with gold could cause a weakening of the oxygen bond strength in the support materials. As a probe to measure the oxygen bond strength in silica and magnesia, the isotopic exchange of molecular oxygen between gas phase and catalyst was employed. Under conditions where both metallic gold (98, 99) and the oxide supports (100) were inactive for the oxygen exchange reaction, a massive exchange of isotopic oxygen was obtained in the case of gold/magnesia and gold/silica catalysts (97). This interaction between gold and oxide supports seems to arise during catalyst preparation when activated oxygen bonds are present in the support materials during the onset of gold nucleation. This phenemenon might be related to the partial stabilization of oxidized gold in high dispersion (1-4). In a comparative study of the oxidation of clean and gold-precovered Si(111) surfaces, it was found that gold catalyzed the formation of silicon tetroxide tetrahedra at room temperature (101). In the absence of gold, only a chemisorbed oxygen monolayer was formed on the silicon surface.

Decomposition Reactions Catalyzed by Gold

Gold surfaces have been the subject of numerous studies of catalytic decomposition with the main emphasis being on the decomposition of hydrogen peroxide and formic acid.

The mechanism of hydrogen peroxide decomposition on gold was investigated by Gossner and Bischof (102), and by Dole *et al.* (103) who measured the isotopic composition of oxygen liberated in the reaction. The presence of superoxide ions (O_2^-) in the aqueous phase during the decomposition of hydrogen peroxide over supported gold indicated the existence of free-radical intermediates (104). The rate-determining step appeared to be the transfer of electrons from gold to hydrogen peroxide (105). Cold-worked gold had higher catalytic activity than annealed gold indicating that the surface terminations of dislocations might play an important role as active sites for the decomposition reaction (106).

In the case of formic acid decomposition, similar conclusions were reached (107, 108, 109), and surface terminations of dislocations similar to conical pits were considered to be the active sites (110). The decomposition of formic acid requires as its limiting step the dissociative chemisorption of the acid leading to a formate as intermediate (111, 112, 113). The apparent activation energy for formic acid decomposition was found to be 50 to 60 kJ/mole (111, 114, 115). Methyl formate gave methanol and carbon monoxide as reaction products of the catalytic decomposition on gold (116).

Gold showed catalytic activity also in the decomposition of nitrous oxide (117, 118, 119), methanol (120) and hydrogen iodide (121). Diazoalkenes were decomposed in the presence of gold yielding polyethylidene (122). Gold exhibited stereospecific regulating properties and produced crystalline polymers (123).

Other Applications of Gold Catalysts

The patent literature contains several claims for gold as a catalyst for vinyl acetate production from ethylene and acetic acid (124). Gold seems also to be active in halogenation and dehalogenation reactions (125, 126). However, not until recently did fundamental studies address the interaction of halogens with gold surfaces (127-132). Interactions between bromine and gold lead to the formation of an adsorbed layer (129, 130) while chlorine adsorption seemed to result in the immediate formation of a surface chloride (132).

There are also numerous applications of gold as electrodes in electrocatalysis, a topic that is not included in this review. Furthermore, this article does not deal with gold as a component in bi- or multimetallic catalysts, and consideration of the rapidly growing literature and the many patents in this field will be reviewed separately in a future issue of this journal.

Monometallic gold catalysts might in many cases not be competitive with other noble metal catalysts in terms of activity. There are, however, instances where gold has the edge over other metals in terms of selectivity. It remains to be clarified to what extent unusual activities and selectivities are related to interactions between gold and oxide support, electron deficiencies on the gold surface sites, lattice distortions and dislocations, and the presence of impurities. Fundamental surface science studies and spectroscopic investigations will hopefully contribute to significant advances in our understanding of the catalytic function of gold.

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Goldsmithing in Ancient Times

Jewellery of the Ancient World BY JACK OGDEN, Trefoil Books, London, 1983, 250 pages, £30

To the metallurgist concerned with gold and its many alloys there is a fascination in the study of the skills and knowledge characteristic of ancient goldsmiths and jewellers, increasing with the greater interest being taken in it in recent years by archaeologists. The present study covers the period from the earliest Egyptian work to the end of the Roman era, a very long phase in which the technology gradually became more sophisticated.

The author, who combines the flair of the connoisseur with the techniques of both the archaeologist and the metallurgist, gives a detailed account of the sources of gold, as well as of silver, copper and tin, in antiquity and then surveys the methods of working the metals and alloys — 'those loveliest secrets and wondrous methods of the great art of goldsmithing' as Benvenuto Cellini wrote, his territory ranging from Persia to Ireland. At the same time he considers the artifacts in the context of the craftsmen who made them and the cultures that produced these men and their work.

In the early periods in Egypt and elsewhere all types of naturally occurring gold alloys, often containing considerable proportions of silver (and then known of course as electrum) were used, but by about the year 2000 B.C. intentional additions of both silver and copper were made in many parts of the Near East and Europe.

Goldsmithing techniques dealt with include not only the obvious methods of sheet metal work, cutting and piercing, engraving, wire and chain making and casting, but also soldering and the ingenious production, by the addition of silver and copper to the gold to yield both lower melting temperatures and appropriate colours, of suitable solders to ensure that the joints were unobtrusive in appearance.

About half of the work deals with gold, the remainder being concerned with gemstones. It concludes with a useful chapter on fakes and forgeries and the techniques employed in their production.

The book is extremely well illustrated with some two hundred black and white photographs and thirty six in colour, almost all of excellent examples of ancient jewellery. There is also an extensive bibliography but, by a regrettable economy on the part of the publisher, the index has been omitted. However, the book forms a major addition to our knowledge of gold metallurgy and fabrication in antiquity, and a tribute to the highly skilled craftsmen of the past.

L.B.H.